

Clustering of vacancy defects in high-purity semi-insulating SiC

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 (Dated: 6th February 2008)

Positron lifetime spectroscopy was used to study native vacancy defects in semi-insulating silicon carbide. The material is shown to contain (i) vacancy clusters consisting of 4–5 missing atoms and (ii) Si vacancy related negatively charged defects. The total open volume bound to the clusters anticorrelates with the electrical resistivity both in as-grown and annealed material. Our results suggest that Si vacancy related complexes compensate electrically the as-grown material, but migrate to increase the size of the clusters during annealing, leading to loss of resistivity.

PACS numbers: 78.70.Bj, 71.60.+z

I. INTRODUCTION

Silicon carbide (SiC) is a promising semiconductor material for high-temperature, high-power, high-frequency and radiation resistant applications. Semi-insulating SiC has shown great potential as a substrate material for SiC- and III-nitride microwave technology. SiC substrates can be made semi-insulating by introducing deep levels (either impurities or intrinsic defects) to the material. High-purity semi-insulating SiC can be grown by the High-Temperature Chemical Vapor Deposition (HTCVD) technique¹, in which pure source gases are used.

Native vacancies have been observed in the material in electron paramagnetic resonance experiments,^{1,2,3,4,5} but their role in the electrical compensation is unclear. Positron lifetime spectroscopy is a method for studying vacancy defects in solid materials.^{6,7} Positrons are repelled by positive ion cores and tend to get trapped at vacancies. Since the electron density in the vacancies is lower than in the bulk, positron lifetime increases and its value indicates the open volume of the defect. Using the relative intensities of different lifetime components, one can determine the concentrations of different vacancy defects.

During the last few years SiC has been extensively studied using positron spectroscopy (see e.g. Refs. 8,9,10, 11,12,13,14,15,16,17,18,19,20,21,22,23,24). These studies often involve irradiated materials. In this paper we use positron lifetime spectroscopy to study as-grown bulk HTCVD 4H-SiC samples, grown under different conditions. We observe clusters of 4–5 vacancies, which grow in size even up to 30 missing atoms after high-temperature annealing. We detect also smaller open volume defects, which we attribute to negative V_{Si} related complexes. Comparison with the results of resistivity measurements shows that the presence of vacancy clusters anticorrelates with the semi-insulating properties of the material. We suggest that the clusters act as neutral agglomeration

centers for the negative vacancy defects causing the high resistivity.

The paper is organized as follows. The details of the positron experiments and theoretical calculations are given in Sec. II. The positron results in the as-grown and high-temperature annealed SiC samples are given and interpreted in Sec. III. In Sec. IV we present the identification of the vacancy defects in the light of theoretical calculations and earlier investigations, and discuss the vacancy concentrations and the effect of vacancy defects on the electrical compensation. Finally Sec. V concludes the paper.

II. METHOD

A. Experimental details

We measured over 20 samples grown by the HTCVD method above 1900 °C in either hydrocarbon rich (type A) or poor (type B) conditions (examples shown in table I). The studied samples are undoped and their impurity levels are $< 10^{16} \text{ cm}^{-3}$ as measured by secondary ion mass spectrometry. Generally all as-grown samples are insulating but sample A1 shows weak n-type conductivity. Post-growth annealings were performed at 1600 °C in H_2 ambient in a CVD reactor. After annealing the resistivity of A-type samples decreased and current-voltage measurements indicated that the samples became more n-type. The type B remain semi-insulating also after annealing.

The samples were measured in darkness between 20–540 K with analog and digital²⁵ positron lifetime spectrometers. The time resolutions of the spectrometers were 240 ps and 215 ps (FWHM), respectively. The digital spectrometer was used for room temperature measurements. The detectors were equipped with plastic scintillators and were positioned in face-to-face geometry in both cases. We used 10 μCi ^{22}Na positron

Table I: Summary of samples studied in this paper. Annealings have been performed at 1600 °C in H₂ ambient. Type A samples are grown in hydrocarbon rich and type B samples in hydrocarbon poor environment. Resistivities are presented at 300 K.

Sample	C ₂ H ₆	Ann.	Resistivity [Ω cm]
A1	rich	0 h	n-type
A1	rich	1 h	n-type
A2	rich	0 h	2×10 ⁹
A2	rich	1 h	1×10 ⁸
A2	rich	2 h	4×10 ⁴ (n)
A2	rich	3 h	5×10 ² (n)
B	poor	0 h	> 10 ¹⁰
B	poor	1 h	> 10 ¹⁰

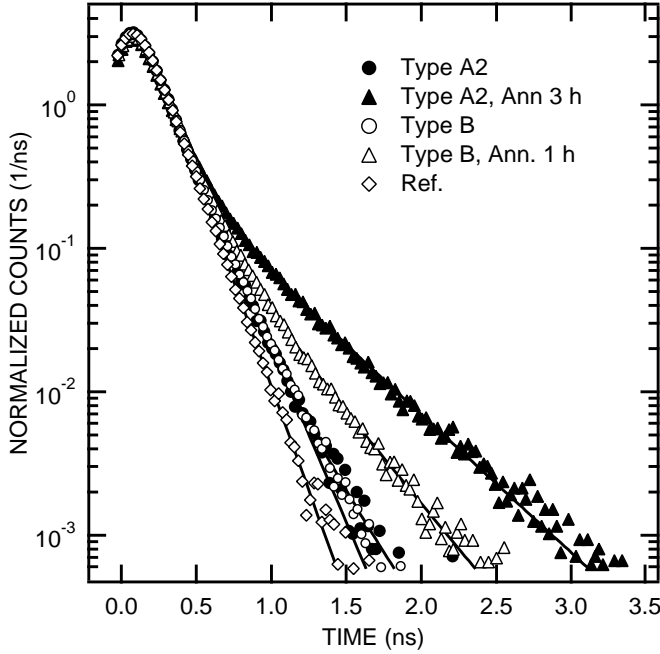


Figure 1: Positron lifetime spectra at 300 K. The solid lines are fits of sums of exponential decay components.

sources deposited on folded 1.5 μm Al foil. Typically $1 - 2 \times 10^6$ counts of annihilation events were collected to each lifetime spectrum. The lifetime spectrum was analyzed as the sum of exponential decay components $\sum_i I_i \exp(-t/\tau_i)$, where the τ_i are the individual lifetime components and I_i their intensities. The increase of the average positron lifetime $\tau_{\text{ave}} = \sum \tau_i I_i$ above the bulk lattice lifetime τ_b shows that vacancy defects are present in the material. The average lifetime τ_{ave} is insensitive to the decomposition procedure, and even as small a change as 1 ps can be reliably measured.

If the samples contain only one vacancy type positron traps with positron lifetime τ_D , the positrons have two different states from which to annihilate, *i.e.* bulk and defect. The longer experimental lifetime component will then be equal to that of the positron lifetime in the defect,

i.e. $\tau_2^{\text{exp}} = \tau_D$. Because of the positrons trapping away from the bulk at rate κ , the shorter experimental lifetime component becomes $\tau_1^{\text{exp}} = (\tau_b^{-1} + \kappa)^{-1}$. This effect can be used to test whether the one-trap model is sufficient to explain the measured data. For more details on the analysis, see *e.g.* refs. 6,7.

B. Theoretical calculations

We calculated theoretically the positron lifetimes in vacancy clusters for the 4H polytype of SiC. For the positron states we used the conventional scheme with the local density approximation (LDA) for electron-positron correlation effects and the atomic superposition method in the numerical calculations.^{26,27} The positron annihilation rate λ is

$$\lambda = \tau^{-1} = \pi r_0^2 c \int d\mathbf{r} |\psi_+(\mathbf{r})|^2 n_-(\mathbf{r}) \gamma[n_-(\mathbf{r})], \quad (1)$$

where n_- is the electron density, ψ_+ the positron wave function, r_0 the classical electron radius, c speed of light, and γ the enhancement factor. We used a modified Boronski-Nieminen enhancement factor,^{28,29} which takes into account lack of complete positron screening in semiconductors. The factor takes form

$$\gamma[n_-(\mathbf{r})] = 1 + 1.23r_s + 0.8295r_s^{3/2} - 1.26r_s^2 + 0.3286r_s^{5/2} + (1 - 1/\epsilon_\infty)r_s^3/6, \quad (2)$$

where r_s is calculated from the electron density as $r_s = \sqrt[3]{3/(4\pi n_-)}$. For the high-frequency dielectric constant in 4H polytype we use value $\epsilon_\infty = 6.78$.^{30,31}

We estimate the sizes of the observed vacancy clusters using these theoretical calculations. The calculated clusters are formed by removing Si-C pairs from the perfect lattice up to the size of 84 atoms. The atoms are removed according to their distance to the "origin" of the cluster (chosen to be the middle point between a Si-C bond, cubic position). The positron state is then solved in $480 - 2N$ atom supercells, where N is the number of Si-C pairs removed.

Because the atoms are simply removed from their ideal positions, the calculated clusters are non-relaxed. In general, the relaxation affects the open volume—and thus the positron lifetime of the clusters. Additionally, the presence of a trapped positron may alter the configuration of the surrounding atoms. According to calculations, lattice relaxations have been found to affect the positron lifetimes in case of V_{Si} in SiC by approximately 12...15 ps and in V_2 by 4...7 ps.²³ Furthermore, the relative effect of relaxations in clusters have been found to diminish to insignificant level in clusters bigger than V_4 in silicon³² (note that the open volume of V_4 in Si is larger than that of V_4 in SiC).

Table II: Samples, their annealing times (at 1600 °C in H₂ ambient), resistivities (at 300 K), positron lifetime values (measured at 300 K), positron trapping rates, vacancy concentrations and cluster sizes. Type A samples are grown in hydrocarbon rich and type B samples in hydrocarbon poor environment. The positron results include the measured average positron lifetime τ_{ave} , the fitted positron lifetime components $\tau_{\{1,2\}}$ and the intensity of the longer lifetime component I_2 . The positron trapping rates to monovacancies κ_1 and to vacancy clusters κ_2 , vacancy defect concentrations for V_{Si}-related defects $[V_{\text{Si}}]$, vacancy clusters $[V_N]$ and cluster sizes N have been determined by the positron annihilation measurements presented. Note that the change of Fermi-Level in type A2 sample evidently changes the charge state (and thus the positron trapping coefficient) of the defects (calculated concentrations *highlighted*).

Sample, annealing time	Resistivity [Ω cm]	τ_{ave} [ps] ± 0.5	τ_1 [ps] ± 2	τ_2 [ps] ± 10	I_2 % ± 2	κ_1 [10^9 s ⁻¹] ± 20 %	κ_2 % ± 20 %	$[V_{\text{Si}}]$ [10^{15} cm ⁻³] ± 20 %	$[V_N]$ [at.] ± 20 %	Cl. Size N ± 20 %
A1	n-type	191	168	284	20	7.5	2.6	120	50	5
A1, 1h	n-type	208	138	350	33	2.1	2.9	30	28	10
A2	2×10^9	163	152	283	8	1.3	0.4	<i>61</i>	<i>8</i>	5
A2, 1h	1×10^8	183	146	406	14	1.4	0.9	<i>66</i>	<i>6</i>	16
A2, 2h	4×10^4 (n)	206	144	440	21	2.0	1.7	<i>33</i>	<i>6</i>	27
A2, 3h	5×10^2 (n)	216	144	451	24	2.4	2.1	<i>39</i>	<i>6</i>	32
B	$> 10^{10}$	164	150	261	13	1.3	0.6	61	15	4
B, 1h	$> 10^{10}$	179	146	342	17	1.4	1.0	69	11	9

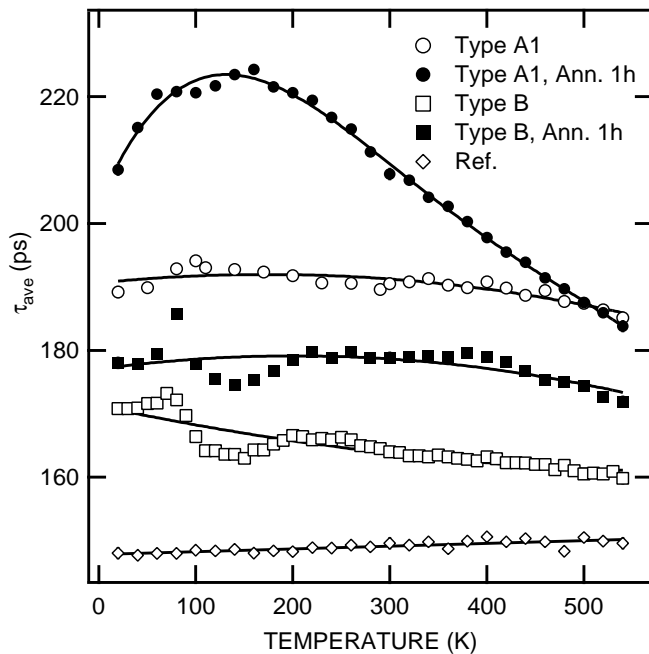


Figure 2: Average positron lifetime as a function of measurement temperature. The solid curves are used for calculation of τ_1^{TEST} (see eq. 3).

III. POSITRON LIFETIME RESULTS

Positron lifetime spectra are shown in Fig 1. The reference sample, p-type bulk SiC, shows only a single lifetime of 150 ps, which we attribute for the positron lifetime τ_b in the SiC lattice. All HTCVD samples have at least two lifetime components.

The lifetime spectra were decomposed into two components. Table II presents the average positron lifetime at 300 K and the two separated components. The inten-

sity of the longer component is also shown. The longer lifetime is 260-290 ps in the as-grown state and increases up to 450 ps after annealing. These lifetime values are typically associated to vacancy cluster consisting of more than two missing atoms.

The positron lifetime measurements as a function of temperature are shown in Fig. 2. We see that the average lifetime above 200 K is constant or decreases with temperature. This suggests that negative vacancies are present in the samples, since positron trapping to negative vacancies decreases with temperature, whereas trapping to neutral vacancies is temperature independent.^{6,7} Below 200 K, especially well seen in the sample A1 Ann, the average lifetime starts to decrease, suggesting the presence of negative ions (residual impurities or intrinsic defects), which act as shallow traps for positrons. The samples B and B Ann have oscillations in τ_{ave} around 100 K, which may reflect some charge transitions in the shallow traps. However, the concentrations of the shallow traps are low compared to those of the vacancy defects, as the decrease of the average lifetime is modest compared to the difference between the average and bulk lifetimes.

Fig. 3 shows the temperature dependence of the positron lifetime components. The positron lifetime at vacancy clusters τ_2 is approximately constant (350 ps or 270 ps) indicating positrons annihilating in a well-defined defect state in each sample. On the other hand, the shorter lifetime τ_1 has a clear tendency to decrease from 160-175 ps at 20 K to 140-150 ps at 500 K. If only the vacancy clusters corresponding to τ_2 were present in the samples, the lifetime τ_1 in the lattice would be related to τ_{ave} , τ_b and τ_2 as

$$\tau_1 = \tau_1^{\text{TEST}} = \tau_b \left(\frac{\tau_2 - \tau_{\text{ave}}}{\tau_2 - \tau_b} \right). \quad (3)$$

The test lifetime τ_1^{TEST} calculated from the experimen-

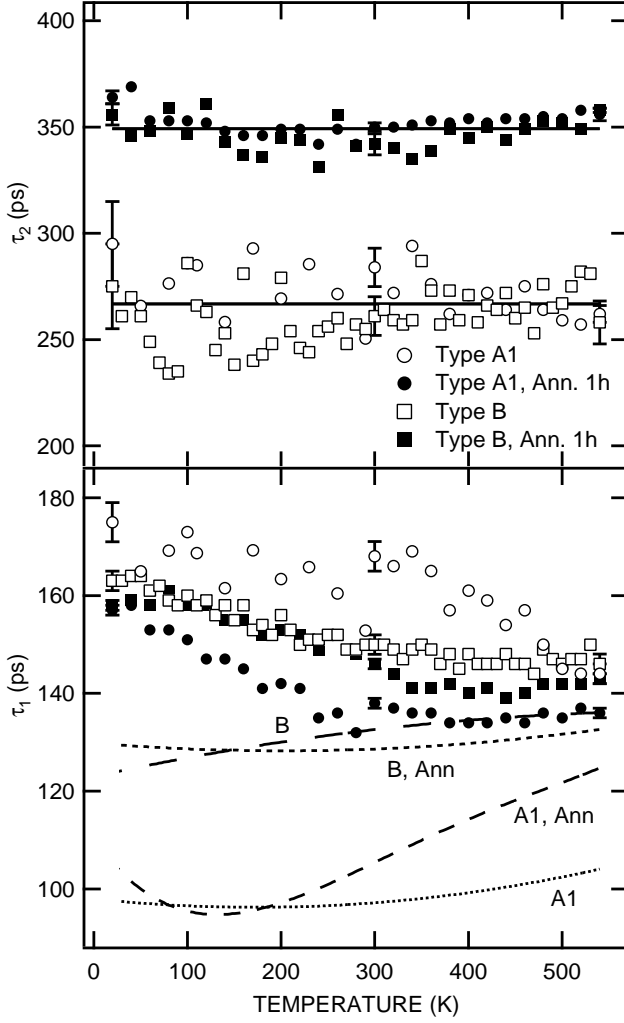


Figure 3: Positron lifetime components vs. measurement temperature. In the lower panel the lines present the parameter τ_1^{TEST} (Eq. 3), which gives information on the number of different vacancy defect species in the samples.

tal values of τ_{ave} , τ_b and τ_2 varies between 95-137 ps and thus it is well below the experimental τ_1 in all samples at any temperature. This means that the vacancy clusters corresponding to τ_2 are not the only defects. There exist also other smaller vacancy defects, which create a lifetime component mixed into the experimental τ_1 lifetime. The smaller defects are especially prominent at low temperatures and their concentration in the sample A1 grown under the hydrocarbon rich condition is high. The positron lifetime at the smaller vacancy defects is estimated to be above 170 ps from the low-temperature part of the Fig. 3. On the other hand, the τ_{ave} vs. T data in Fig. 2 indicates that the defect-specific lifetime is below 220 ps.

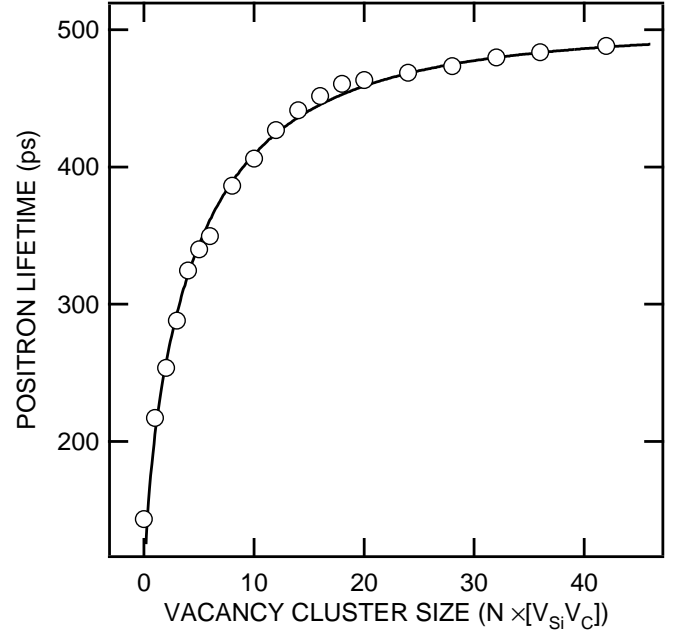


Figure 4: Calculated positron lifetimes in vacancy clusters in 4H SiC. The solid line is used for determining the cluster sizes from the measured τ_2 . It is worth noticing that the sensitivity of the positron lifetime on the vacancy cluster size is significantly reduced when the cluster size exceeds 10 missing Si-C pairs.

IV. DISCUSSION

A. Identification of the vacancy defects

1. Vacancy clusters

The measured lifetime τ_2 is longer than that determined earlier (typical values reported in literature shown in parenthesis, see more discussion about lifetime values at the end of this section) for the carbon vacancy V_C (≤ 160 ps), the silicon vacancy V_{Si} (180-210 ps), or divacancy (~ 250 ps) in SiC. The electron density in the defect is thus lower, indicating that the observed defects are vacancy clusters.

The calculated positron lifetimes in vacancy clusters are presented in figure 4. The results obtained are similar to those reported earlier for 3C and 6H SiC.¹⁰ Our calculations give for the positron lifetime in bulk SiC a value of $\tau_b = 143.7$ ps, in agreement with the measured value $\tau_b = 149.6$ ps. When using the theoretical calculations to determine the measured cluster sizes, we compare the differences between the bulk and defect lifetimes.

According to the theoretical calculations, a measured positron lifetime of 260 ps observed in as-grown samples corresponds to a vacancy cluster V_4 (2 Si-C molecules removed). The lifetime of 350 ps, detected after annealing, is expected for an open volume of a cluster V_{10} . The estimated cluster sizes in different samples are presented

in Table II. We observe that the cluster sizes increase in the annealings from the size of roughly 5 missing Si-C pairs in the as-grown material up to 30 missing Si-C pairs in the sample annealed for 3 hours. These approximate values represent the averages of the open volume distribution of vacancy clusters. This may mean various different cluster sizes or possibly a "magic" cluster size, in which the number of dangling bonds are minimized, as shown in e.g. Si and GaAs.^{32,33} Clustering of vacancies due to annealing has been previously reported in n-type 6H SiC after neutron- and ion irradiation.^{19,34,35}

2. Si vacancy related defects

The estimated lifetime of the positrons trapped at the smaller observed vacancy defects is $\tau_V = 195 \pm 25$ ps range, *i.e.* $\tau_V - \tau_b = 20 \dots 70$ ps. In order to identify this defect, we need to consider the different lifetime values that have been associated with different aspects of SiC. Reported positron lifetimes (both experimental and theoretical) for bulk material range between 134 and 150 ps. The lifetime values associated with different vacancy defects vary clearly more.

For 4H polytype, bulk lifetime values including 141 ps³⁶, 145 ps⁹ 150 ps²¹, and for 3C-SiC 140 ps have been reported.¹⁷ The most common polytype encountered in recent positron studies for SiC is 6H, for which several values for bulk lifetime have been proposed, in the range 136...150 ps.^{8,14,15,16,18,20,21,22} The theoretical calculations give lifetimes of 134 ps for 4H-SiC²³, 141 ps for 6H-SiC and 138 for 3C-SiC.¹¹ It should be noted that different calculation schemes (especially different enhancement factors) cause differences in the resulting absolute lifetimes, which becomes evident when comparing results from different studies.²³ Somewhat similar situation applies to experimental values (e.g. due to differences in measurement geometry, energy windows or source corrections). Thus, in comparisons between different lifetime values obtained from different studies, we compare preferably the differences between determined lifetime values in defects and bulk ($\tau_V - \tau_b$), rather than focus solely on the absolute values of the lifetimes.

The studies of positrons trapping in vacancy-type defects are typically performed by making use of irradiation, and the identification of the defects is often based on comparing the measured and the theoretical positron lifetime values. The reported values for positron lifetimes in V_{Si} based on irradiation experiments are typically around $\tau_V = 200$ ps, in the range $\tau_V - \tau_b = 14 \dots 116$ ps.^{8,14,15,17,22,37} Theoretical calculations reported in the literature predict $\tau_V - \tau_b = 47 \dots 64$ ps in 4H and 6H SiC^{11,23} for V_{Si} . For V_C values of $\tau_V - \tau_b = 8$ and 16 ps have been reported^{14,37} and theory gives $\tau_V - \tau_b = 6 \dots 12$ ps.^{11,23}

In addition to the previous values, lifetime differences in the range $\tau_V - \tau_b = 65 \dots 94$ ps have been reported in irradiated samples.^{12,20,22,24} The experimental values

reported^{8,15} $\tau_V - \tau_b = 80 \dots 83$ ps for the divacancy ($V_{Si}V_C$) are in good agreement with the reported theoretical predictions $\tau_V - \tau_b = 73 \dots 75$ ps for 4H²³ and 6H¹¹ SiC.

Vacancies are often detected also in as-grown materials. In many cases the lifetime values are somewhat longer than the values found after irradiation. Lifetime values mainly in the range 250...350 ps ($\tau_V - \tau_b = 100 \dots 200$ ps) have been observed in as-grown SiC samples.^{13,14,16,21} Also smaller values of $\tau_V - \tau_b = 50 \dots 75$ ps have been reported¹⁸ and attributed to V_{Si} and $V_{Si}V_C$. According both to our and earlier reported¹⁰ theoretical calculations, a lifetime of 250 ps corresponds to open volume of at least similar size with that of V_4 , *i.e.* $(V_{Si}V_C)_2$.

In the light of the lifetime values discussed previously, the possible candidates for the smaller vacancy defects observed here are thus monovacancies or monovacancy related complexes in the Si and C sublattices and small clusters with at most 2-3 missing atoms. Several arguments point in the direction that the observed defects are related to V_{Si} rather than V_C . The main point is that, as shown above, the lifetime of the smaller vacancy defect is ≥ 170 ps, *i.e.* above all presented estimates for the carbon vacancy V_C . In addition, the C vacancy in semi-insulating SiC could be positively charged according to theoretical calculations³⁸ and EPR experiments⁵ and thus repulsive to positrons. Hence we attribute the defect responsible for the increase of τ_1 at low temperature to the Si vacancy or a complex involving V_{Si} . This conclusion is in agreement with the EPR and infrared absorption results,^{1,4,5} which suggest that samples similar to A1 contain V_{Si} , whereas samples of type B have positive C vacancies, and also V_{Si} but less than in a sample like A1. Absorption measurements¹ further show that the concentration of V_{Si} -related center T_{V2a} ⁴ decreases in annealing of A-type samples, which correlates with the behavior of τ_1 in Fig. 3. However, based on our positron measurements only, we cannot rule out the possibility of the defect being *e.g.* the divacancy $V_{Si}V_C$.

It is interesting that the Si vacancy related defects are prominent at low temperatures, whereas the larger vacancy clusters dominate the positron lifetime spectrum at high measurement temperatures. Positron trapping at neutral defects is independent of temperature, whereas the negative defects become stronger positron traps at lower temperatures.^{6,7} Hence, the temperature dependence of the lifetime components suggests that the observed Si vacancy related defects act as acceptors in SI HTCVD SiC, but the vacancy clusters are electrically neutral. In the annealed A1 type sample, however, the average positron lifetime decreases with the increasing temperature. This means evidently that a part of the clusters in the *n*-type material are negatively charged.

B. Vacancy defect concentrations

The vacancy defect concentrations can be estimated from the positron trapping model using the decomposed lifetimes and intensities. In the calculation we assume that both vacancy clusters (CL) and vacancies in Si-sublattice (V) are present and the positron lifetimes at the vacancies in the Si-sublattice and in the bulk SiC are intermixed to the component τ_1 . The positron trapping rates κ are^{6,7}

$$\kappa_V = \frac{\tau_1(\tau_b^{-1} - I_2\tau_2^{-1}) - I_1}{(\tau_V - \tau_1)}, \quad (4)$$

$$\kappa_{CL} = \frac{I_2}{I_1}(\tau_b^{-1} - \tau_{CL}^{-1} + \kappa_V). \quad (5)$$

The positron lifetime for the vacancy cluster is taken directly from the decomposition as $\tau_{CL} = \tau_2$. For the positron lifetime at the Si vacancy related defects we use $\tau_V = 195$ ps, which is in the middle of our range determined for the lifetime of the smaller defect. Values close to this are also often attributed for the positron lifetime in V_{Si} (see section IV A 2). The defect concentrations can be obtained from the trapping rates κ as $c = \kappa N_{at}/\mu$. Here $N_{at} = 9.64 \times 10^{22} \text{ cm}^{-3}$ is the atomic density of SiC.

Positron trapping coefficients for negative vacancies at 300 K range typically between $0.5..5 \times 10^{15} \text{ s}^{-1}$ in semiconductors.⁶ For instance, a value of $\mu_V^- = 1.1 \times 10^{15} \text{ s}^{-1}$ has been reported for $V_{Si}VC^{15}$ in SiC at room temperature. Also, coefficient as high as $6 \times 10^{16} \text{ s}^{-1}$ have been reported for V_{Si}^- in SiC.¹⁷ We consider the latter value to be much too high, as the typical coefficients reported for semiconductors are an order-of-magnitude less. It should be noted, however, that determining the values for the trapping coefficient μ is not an easy task and thus one should consider the possibility of the coefficient differing even by factor 2-3 from the physically proper value. Using an inaccurate trapping coefficient would thus affect the determined absolute defect concentrations (linearly). Still, the error would be similar in all samples and the comparison of the concentrations between different samples is possible.

Due to high uncertainties associated for the value of μ_V , we use positron trapping coefficient at 300 K $\mu_V^- = 2 \times 10^{15} \text{ s}^{-1}$ for singly negative vacancies in Si sublattice, which is a typical value in wide band-gap semiconductors.⁶ For neutral vacancies we use $\mu_V^0 = 1 \times 10^{15} \text{ s}^{-1}$, since the trapping coefficients of the neutral and negative mono- and divacancies in Si have been found to differ by a factor of 1.5-3.5.^{7,39,40} In n-type samples we use a value $3\mu_V^-$, since theoretical calculations predict that V_{Si} changes its charge state from 1^- to 2^- , and eventually to 3^- , when the Fermi level approaches the conduction band.³⁸ This change of charge state of V_{Si} is likely to occur in the sample A2, where the conductivity of the sample changes from semi-insulating to

n-type, indicating the movement of the Fermi level. No change in the conductivity of samples A1 and B was observed. For small vacancy clusters (transition limited positron trapping), the positron trapping coefficient for vacancy clusters of n vacancies can be approximated as $\mu_{CL} = n\mu_V$.⁴¹ As can be observed in Fig. 2, a part of the vacancy clusters in the annealed sample A1 are likely to be negative, which increases the overall trapping coefficient of the clusters. Hence the concentration of the vacancy clusters in the annealed sample A1 is probably a bit overestimated. The determined vacancy defect concentrations are summarized in Table II, being in the mid- 10^{16} cm^{-3} for the Si vacancy related defects and $10^{15} - 10^{16} \text{ cm}^{-3}$ for the vacancy clusters.

The experimental vacancy defect concentrations and sizes (Table II) suggest the following interpretation: Annealings of the samples of type A, grown under hydrocarbon rich conditions, increase the sizes of the vacancy clusters from approximately 5 to about 30 vacancies, with a simultaneous decrease of the cluster concentration. The Si vacancy complex concentration is also lowered by the annealing of the n-type sample A1. Thus we suggest that annealing causes V_{Si} to (partly) agglomerate to the vacancy clusters by migration.

In the originally semi-insulating sample A2, the trapping rate κ_1 of positrons to the V_{Si} -related defects increases roughly by a factor of two. However, the annealing decreases the resistivity of the sample (towards n-type conductivity), which indicates that the Fermi level moves towards the conduction band. This is likely to induce an increase of the negativity of the V_{Si} , which would increase the trapping coefficient to these vacancies by a factor of 2-3, depending on the initial and final charge states. Hence the concentration of the V_{Si} -related defects decreases during the annealing. However, it is worth noticing that the estimation of the concentration of the V_{Si} -related defects is less accurate than in the sample A1 due to the likely change in the charge state of the defects. Interestingly, the total open volume increases in the annealing of the A-type sample. Based on these observations, we suggest that the annealing causes V_{Si} to agglomerate to the clusters.

Annealing increases the average size of the vacancy clusters also in the sample of type B, grown under hydrocarbon poor conditions. The concentration of the V_{Si} -related defects is not significantly changed in the annealing.

C. Electrical compensation

The positron results lead to several important conclusions regarding the origin of the semi-insulating properties of the material. The temperature dependence of the average positron lifetime (Fig. 2) shows that the samples of both types A and B do not contain significant concentrations of negative ions, such as impurities or negative interstitials or antisite defects. These types of defects

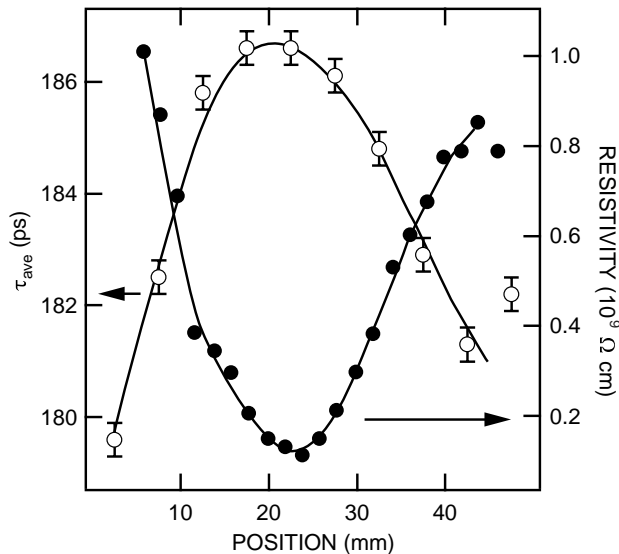


Figure 5: Average positron lifetime and resistivity as a function of position on the diameter of a 2" type A wafer. The lines are for guiding the eye.

thus contribute little to the electrical compensation, at maximum at the level of their detection limit; their concentration is at most in the mid- 10^{15} cm^{-3} range. This observation correlates also with low concentrations of B and Al acceptors ($< 5 \times 10^{15} \text{ cm}^{-3}$ and $< 5 \times 10^{14} \text{ cm}^{-3}$, respectively) measured with secondary ion-mass spectrometry.

The samples grown in hydrocarbon rich conditions (type A) are either slightly n-type already after the growth, or lose their high resistivity after annealing. The detected negative V_{Si} -related complex is an obvious candidate for the compensating intrinsic defect in as-grown material. Hence the n-type character of the annealed samples can be explained by the loss of compensation due to migration of negative V_{Si} to primarily neutral vacancy clusters. It is worth noticing that a part of the vacancy clusters turn negative in the annealing of the sample A1. This does not affect the interpretation that the compensation is weakened due to the migration of V_{Si} to the clusters, however, as the negativity implies that the cluster concentration presented in Table II overestimates the "proper" value.

The concentration of the vacancy clusters should thus increase with the decreasing resistivity of HTCVD SiC. To verify this relation in the as-grown samples, we measured positron lifetime and resistivity as a function of position in a strip like sample, cut diagonally across a wafer grown in hydrocarbon rich growth conditions (type A). The lifetime component $\tau_2 = 247 \pm 10 \text{ ps}$ remained constant over the sample, indicating constant vacancy cluster size (≈ 4 atoms). As can be seen in Fig. 5, the average positron lifetime and the resistivity of the sample anticorrelate. The change of τ_{ave} is caused by the vari-

ation in the intensity I_2 and thus the positron trapping rate at the vacancy clusters. The concentration of the clusters thus decreases with increasing resistivity of the material, most likely since less compensating V_{Si} -related complexes have migrated to the neutral vacancy clusters during the growth. Unfortunately, the direct analysis of the concentrations of V_{Si} -related defects using eqs. 4 and 5 is not possible in the case of the data of Fig. 5, since (i) the changes of the average lifetime are small, only about 6 ps, (ii) the single-trap model is almost valid (*i.e.* the concentration of the V_{Si} related defects is barely above the sensivity limit 10^{16} cm^{-3}) and (iii) the differing position of the Fermi-level may have an influence on the charge state of V_{Si} -related defects.

The annealing of samples grown under hydrocarbon poor conditions (type B) leads to growth of the vacancy clusters, but the concentration of the smaller defects is not substantially changed. This suggests that in B-type material the Si vacancies have transformed (or belong to) to more stable complexes, such as the $V_{\text{C}}\text{C}_{\text{Si}}$ ^{42,43}, or divacancies⁴⁴, which remain as compensating centers after the annealing. It is also possible that the high resistivity of type B samples could also be dominated by the C vacancy,^{2,3,5,45,46} which is more stable than V_{Si} according to calculations.^{42,47}

V. CONCLUSIONS

Positron lifetime measurements in semi-insulating HTCVD SiC samples reveal vacancy clusters of the size of 4–5 missing atoms. Their charge state in the semi-insulating material is neutral. The clusters grow in size to about 30 missing atoms in post-growth annealings at 1600 °C. Positron experiments identify also Si vacancy related smaller complexes, which are negatively charged. They partly disappear during annealing in materials grown under hydrocarbon rich conditions. After annealing the materials become more n-type, as part of the compensation is lost by the migration of Si vacancy related defects to (partially) increase the size of the open volume of clusters. Hence, our results suggest that the Si vacancy complexes act as compensating centers partly responsible for the insulating properties of high purity HTCVD SiC. This conclusion is supported by the measurement of resistivity variations across a SiC wafer, which shows that concentration of the vacancy clusters anticorrelates with the resistivity.

Acknowledgments

One of the authors (R.A.) gratefully acknowledges the support from Finnish Academy of Science and Letters, Vilho, Yrjö and Kalle Väisälä Foundation.

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- ¹ A. Ellison, B. Magnusson, C. Hemmingsson, W. Magnusson, T. Iakimov, L. Storasta, A. Henry, N. Henelius, and E. Janzén, Proc. of MRS fall meeting 2000 **640**, H1.2 (2001).
 - ² M. E. Zvanut and V. V. Konovalov, Appl. Phys. Lett. **80**, 410 (2002).
 - ³ V. V. Konovalov, M. E. Zvanut, and J. van Tol, Phys. Rev. B **68**, 012102 (2003).
 - ⁴ N. T. Son, Z. Zolnai, and E. Janzén, Phys. Rev. B **68**, 205211 (2003).
 - ⁵ N.T. Son, B. Magnusson, Z. Zolnai, A. Ellison, and E. Janzén, Materials Science Forum **433-436**, 45 (2003).
 - ⁶ R. Krause-Rehberg and H.S. Leipner, *Positron Annihilation in Semiconductors: Defect Studies*, Springer Series in Solid-State Sciences (Springer-Verlag, Berlin Heidelberg, 1998).
 - ⁷ P. Hautojärvi and C. Corbel, in *Positron Spectroscopy of Solids* (North Holland publishing company, Amsterdam, New York, Oxford, 1993), vol. CXXV of *Proceedings of the International School of Physics "Enrico Fermi"*.
 - ⁸ S. Arpiainen, K. Saarinen, P. Hautojärvi, L. Henry, M.-F. Barthe, and C. Corbel, Phys. Rev. B **66**, 075206 (2002).
 - ⁹ W. Bauer-Kugelmann, G. Kögel, P. Sperr, and W. Triftshäuser, Materials Science Forum **255-257**, 662 (1997).
 - ¹⁰ G. Brauer, W. Anwand, P. G. Coleman, J. Störmer, F. Plazaola, J. Campillo, Y. Pacaud, and W. Skorupa, J. Phys. Condens. Matter **10**, 1147 (1998).
 - ¹¹ G. Brauer, W. Anwand, E.-M. Nicht, J. Kuriplach, M. Šob, N. Wagner, P. Coleman, M. J. Puska, and T. Korhonen, Phys. Rev. B **54**, 2512 (1996).
 - ¹² G. Brauer, W. Anwand, P. G. Coleman, A.P. Knights, F. Plazaola, Y. Pacaud, W. Skorupa, J. Störmer, and P. Willutzki, Phys. Rev. B **54**, 3084 (1996).
 - ¹³ D. Britton, M. Barthe, C. Corbel, A. Hempel, L. Henry, P. Desgardin, W. Bauer-Kugelmann, G. Kögel, P. Sperr, and W. Triftshäuser, Appl. Phys. Lett. **78**, 1234 (2001).
 - ¹⁴ S. Dannefaer, D. Craigen, and D. Kerr, Phys. Rev. B **51**, 1928 (1995).
 - ¹⁵ L. Henry, M.-F. Barthe, C. Corbel, P. Desgardin, G. Blondiaux, S. Arpiainen, and L. Liskay, Phys. Rev. B **67**, 115210 (2003).
 - ¹⁶ A. Kawasuso, H. Itoh, S. Okada, and H. Okumura, J. Appl. Phys. **80**, 5639 (1996).
 - ¹⁷ A. Kawasuso, H. Itoh, N. Morishita, M. Yoshikawa, T. Ohshima, I. Nashiyama, S. Okada, H. Okumura, and S. Yoshida, Appl. Phys. A **67**, 209 (1998).
 - ¹⁸ C. Ling, A. Deng, S. Fung, and C. Beling, Appl. Phys. A **70**, 33 (2000).
 - ¹⁹ A. Mokrushin, A. Girka, and A. Shiskin, Phys. Stat. Sol. A **128**, 31 (1991).
 - ²⁰ A. Polity, S. Huth, and M. Lausmann, Phys. Rev. B **59**, 10603 (1999).
 - ²¹ W. Puff, M. Boumerzoug, J. Brown, P. Mascher, D. MacDonald, P. Simpson, A. Balogh, H. Hahn, W. Chang, and M. Rose, Appl. Phys. A **61**, 55 (1995).
 - ²² A. Rempel and H.-E. Schafer, Appl. Phys. A **61**, 51 (1995).
 - ²³ T. Staab, L. Torpo, M. Puska, and R. Nieminen, Materials Science Forum **353-356**, 533 (2001).
 - ²⁴ A. Uedono, H. Itoh, T. Ohshima, R. Suzuki, T. Ohdaira, S. Tanigawa, Y. Aoki, M. Yoshikawa, I. Nashiyama, T. Mikado, et al., Japanese Journal of Applied Physics **36**, 6650 (1997).
 - ²⁵ J. Nissilä, K. Rytölä, R. Aavikko, A. Laakso, K. Saarinen, and P. Hautojärvi, Nucl. Instr. & Meth. A **538**, 778 (2005).
 - ²⁶ M. Puska and R. Nieminen, J. Phys. F **13**, 333 (1983).
 - ²⁷ M. Puska and R. Nieminen, Reviews of Modern Physics **66**, 841 (1994).
 - ²⁸ E. Boronski and R. Nieminen, Phys. Rev. B **34**, 3820 (1986).
 - ²⁹ M. Puska, J. Phys. Condens. Matter **3**, 3455 (1991).
 - ³⁰ P. Shaffer, Applied Optics **10**, 1034 (1971).
 - ³¹ H. Mutschke, A. Andersen, D. Clément, T. Henning, and G. Peiter, Astron. Astrophys. **245**, 187 (1999).
 - ³² T. E. M. Staab, M. Haugk, T. Frauenheim, and H. S. Leipner, Phys. Rev. Lett. **83**, 5519 (1999).
 - ³³ D. Chadi and K. Chang, Phys. Rev. B **38**, 1523 (1988).
 - ³⁴ W. Anwand, G. Brauer, D. Pankin, and W. Skorupa, Materials Science Forum **363-365**, 442 (2001).
 - ³⁵ W. Anwand, G. Brauer, H. Wirth, W. Skorupa, and P. Coleman, Applied Surface Science **194**, 127 (2002).
 - ³⁶ S. Dannefaer, V. Avalos, and R. Yakimova, Materials Science Forum **483-485**, 481 (2005).
 - ³⁷ S. Dannefaer and D. Kerr, Diamond and Related Materials **13**, 157 (2004).
 - ³⁸ L. Torpo, M. Marlo, T.E.M. Staab, and R.M. Nieminen, J. Phys. Condens. Matter **13**, 6203 (2001).
 - ³⁹ P. Mascher, S. Dannefaer, and D. Kerr, Phys. Rev. B **40**, 11764 (1989).
 - ⁴⁰ J. Mäkinen, P. Hautojärvi, and C. Corbel, J. Phys. Condens. Matter **4**, 5137 (1992).
 - ⁴¹ R. Nieminen and J. Laakkonen, Appl. Phys. **20**, 181 (1979).
 - ⁴² M. Bockstedte, A. Mattausch, and O. Pankratov, Phys. Rev. B **69**, 235202 (2004).
 - ⁴³ T. Lingner, S. Greulich-Weber, J.-M. Spaeth, U. Gerstmann, E. Rauls, Z. Hajnal, T. Frauenhaim, and H. Overhof, Phys. Rev. B **64**, 245212 (2001).
 - ⁴⁴ N. T. Son, P. Carlsson, J. ul Hassan E. Janzén, T. Umeda, J. Isoya, A. Gali, M. Bockstedte, N. Morishita, T. Ohshima, and H. Itoh, Phys. Rev. Lett. **96**, 055501 (2006).
 - ⁴⁵ N. T. Son, B. Magnusson, Z. Zolnai, A. Ellison, and E. Janzén, Materials Science Forum **457-460**, 437 (2004).
 - ⁴⁶ B. Magnusson, R. Aavikko, K. Saarinen, N. Son, and E. Janzén, Materials Science Forum (2006), to be published.
 - ⁴⁷ E. Rauls, T. Frauenheim, A. Gali, and P. Deak, Phys. Rev. B **68**, 155208 (2003).